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FEASIBILITY OF CONTINUOUS  
FORMING OF BORON  
CARBIDE MONOFILAMENTS

Final Report  
(Contract NsG-680)

By

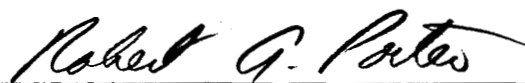
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Prepared for:

National Aeronautics & Space Administration  
Washington, D. C.

28 January 1965

Approved:

  
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## INTRODUCTION

This report concerns an experimental investigation of the feasibility of producing boron carbide fibers by a continuous coating technique. Carbon filaments were used as the substrate for the deposition of boron carbide.

Low-density, high-strength monofilaments are of considerable interest to NASA and the Air Force as high modulus reinforcements in the structure of composites for applications such as rocket motor cases, aircraft and space vehicle structures, as well as aircraft gas turbine engines. Today these fibers are made by decomposition of boron halides on an incandescent tungsten filament. A boron carbide coated carbon filament would provide a substantial decrease in the density of such filaments.

Boron carbide was selected as a candidate material for producing filaments because of its low cost relative to boron and because of its low density, high melting point, high strength, relatively high electrical conductivity, and high modulus of elasticity. These and other physical properties are listed in Table 1.

TABLE I

BORON CARBIDE PROPERTIES\*

Density (apparent specific gravity 2.52 gm/cc)	99 <sup>+</sup> % of theoretical
Hardness (Knoop 100)	2800
Porosity	impermeable
Melting Point	4350°F
Working Temperature	
Inert Atmosphere	4100°F max.
Oxidizing Atmosphere	1000°F max.
Thermal Expansion in/in/°F	$3.22 \times 10^{-6}$
Thermal Conductivity (BTU/sq. ft./in./hr./°F at 70°F)	188
Modulus of Rupture (psi)	
70°F	$50 \times 10^3$
1200°F	$42 \times 10^3$
2000°F	$35 \times 10^3$
Modulus of Elasticity (psi)	
70°F	$65 \times 10^6$
Compressive Strength	$42 \times 10^4$

\* The Carborundum Company  
Niagara Falls, New York

### SUMMARY

1. Boron carbide has been melted on a water-cooled copper hearth in an argon atmosphere, using an induction generator at a frequency of 450 kilocycles per second.
2. A partial coating of boron carbide has been produced on a carbon filament by drawing it through molten boron carbide.
3. The major variable in the coating process has been isolated and identified as the dwell time of the fiber within the melt.

## METHOD OF APPROACH

The technique proposed for the production of boron carbide fibers involves the reaction of molten boron carbide with a carbon filament to form a coating.

In general, the proposed technique consists of passing a carbon filament through a melt of boron carbide. The boron carbide was to be inductively melted on a water-cooled, copper hearth (1) within an inert atmosphere. Thus, the problem of contamination encountered when molten boron carbide is prepared by conventional furnacing in refractory containers by either arc or induction techniques is avoided.

The method was conceived from work conducted by Kuhn and Lambertson on the synthesis of boron carbide and boron nitride (2) and an investigation of "cold" crucible melting and casting of boron carbide.



## EXPERIMENTAL PROCEDURES

All experiments conducted at Spindletop Research involving the melting of boron carbide using induction apparatus employed a Lepel, Type 2 CMU, 30-kilowatt, 450-kilocycle power source.

### PHASE A

Preliminary experimental work was done with high boron, boron carbide powder of mesh size #325 and finer. (3) Using a solid copper hearth of 5/8-inch diameter, a series of tests were run to determine if a coil configuration sufficient to couple to the boron carbide powder could be found. To provide for more effective utilization of the generator output, a load coil transformer (4) designed to effect an impedance match between generator and small, 1- to 4-turn coils was used.

It was found that melting of the boron carbide powder could only be accomplished with the aid of a graphite "susceptor"; that is, by transferring the heat generated in the graphite to the boron carbide powder. The particular susceptor employed for this first melt consisted of a graphite disc, 5/8-inch in diameter and 1/16-inch thick, placed concentrically on the hearth but thermally insulated from the hearth by carbon felt, and a compact of boron carbide 1/4-inch thick placed on the disc. This arrangement was confined within a fused silica tube 1-1/16-inch OD and 15/16-inch ID with nitrogen used as a flush gas.

Coil configuration was two turns of 1/4-inch OD copper tubing with 1-3/8-inch ID connected directly to the load coil transformer. Generator tank coil tap was adjusted for maximum power output.

The melts obtained using these methods were unsatisfactory for fiber coating experiments since the boron carbide powder only partially melted. This was, however, the first experimental verification of the difficulties associated in inductively coupling to boron carbide.

A further objective of these experiments was to attempt sintering the boron carbon powder between two susceptors

and use the resulting boron carbide compact for melting experiments on the hearth. It was found, however, that the boron carbide could not be sintered in this manner at temperatures below the melting point of boron carbide. Furthermore, if the boron carbide was allowed to melt, it reacted with the graphite disc and thereby contaminated it. Efforts were also made to eliminate the carbon felt and still effect melting. With the coil arrangement described, it was not possible to heat to red heat even a single graphite disc on the cold hearth.

#### PHASE B

A series of experiments were conducted to provide an insight into some of the problems associated with placing a carbon filament into molten boron carbide.

The apparatus described in Phase A was modified to include use of:

- 1) 4-turn heating coil made from 1/4-inch OD copper tubing with 1-3/8-inch ID and 1-1/2-inch high
- 2) Cylindrical graphite crucibles 1-1/2-inch high and 5/8-inch OD with an internal bore 3/8-inch and 1-3/16-inches deep
- 3) Argon flush gas
- 4) 0.006-inch D x 8-1/2-inch long carbon filaments (5)

Boron carbide powder was manually packed to fill all of the crucible bore and placed concentrically on the cold hearth. It was found to be relatively easy to completely melt the entire powder charge as evidenced by sectioning the crucible upon cooling. It was further found that the cooled crucible had been boron carbide coated well above the melt line, indicating creeping. Similar experiments clearly indicated reaction of the molten boron carbide with the crucible; prolonged maintenance of the melt within the crucible led to complete penetration of the liquid boron carbide through the crucible wall.

Examination of fibers dipped into the melt and withdrawn always revealed a reaction of the fiber with the melt. This was evidenced by microscopic examination of the "filament-ends" revealing a gradual tapering down to a fine point. A representative example of this tapering is shown in Figure 1. It is important to emphasize that the dwell time of the filament-end in the melt was on the order of one second. Efforts to decrease this dwell time were not successful due to a lack of manual control of fiber position because of cantilever vibration in the dipping process.

#### PHASE C

The type of crucible used in B was modified to have the bottom open to the cold hearth. Crucibles packed with boron carbide powder and placed on the cold hearth were found to have provided essentially the same melt characteristics found in Phase B. It was observed, however, that the bottom 1/8 inch of boron carbide powder charge next to the hearth did not melt or sinter but remained as a powder. Several attempts were made to withdraw the tube-type crucible while the boron carbide was molten, the idea being that it may have been possible to leave the molten boron carbide intact on the cold hearth in a molten state. However, it was always found that the boron carbide accompanied the crucible during withdrawal.

#### PHASE D

A series of experiments were designed with the sole intent to melt boron carbide on a cold hearth within an inert atmosphere. Equipment design was not to be influenced by the accessibility of the melt to fiber insertion. Further use of boron carbide powder was discontinued. Instead, we obtained solid hot pressed boron carbide discs 7/8-inch D and 1/4-inch thick with an average density of 2.43 gm/cc. (6) Based on information supplied by the Lepel High Frequency Laboratories, a special plate-concentrator coil was constructed as shown in Figure 2. A new copper hearth was constructed with 7/8-inch D to accept the boron carbide disc. The plate-concentrator coil was connected directly to the generator output. Schematic arrangement of the melting apparatus is shown in Figure 3.

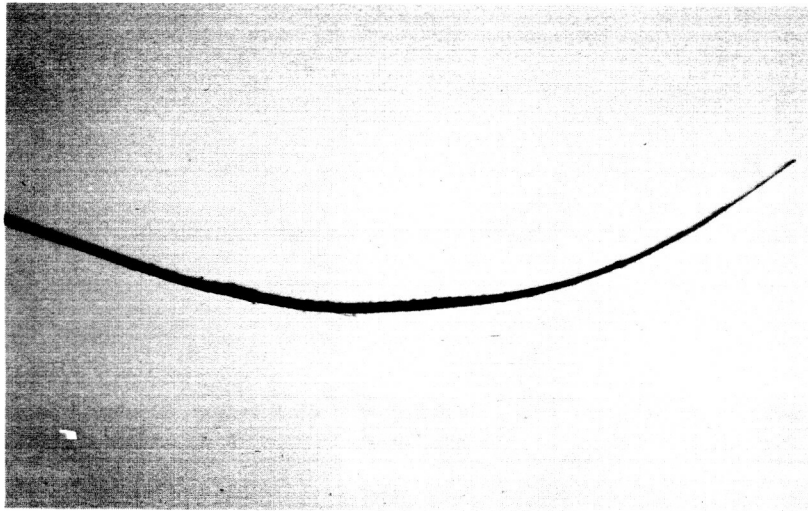
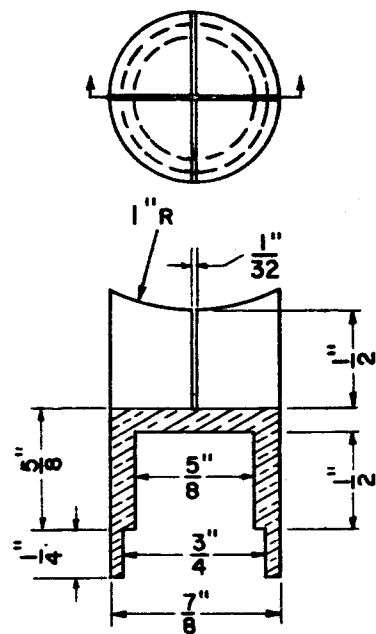
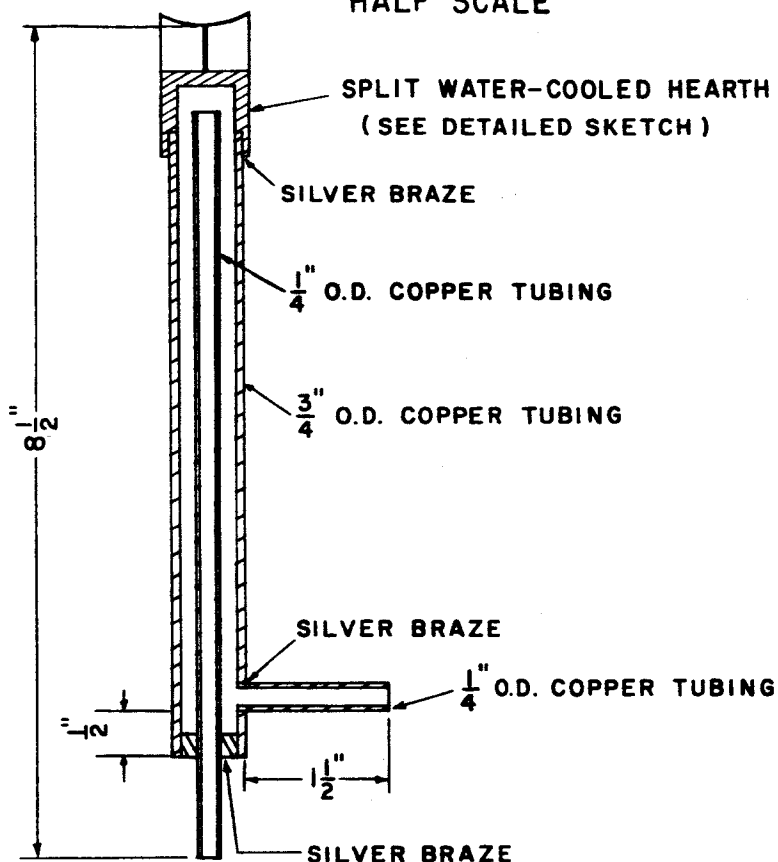


FIGURE 1. CARBON FIBER (0.006-IN. DIAMETER)  
DIPPED IN GRAPHITE CRUCIBLE MELT  
OF BORON CARBIDE FOR APPROXIMATELY  
ONE SECOND. MAGNIFIED 6.5 TIMES.

# FIG.2- PLATE CONCENTRATOR & SPLIT WATER-COOLED HEARTH

## SPLIT WATER-COOLED HEARTH ASSEMBLY

HALF SCALE



SPLIT WATER-COOLED HEARTH  
(DETAIL)  
FULL SCALE

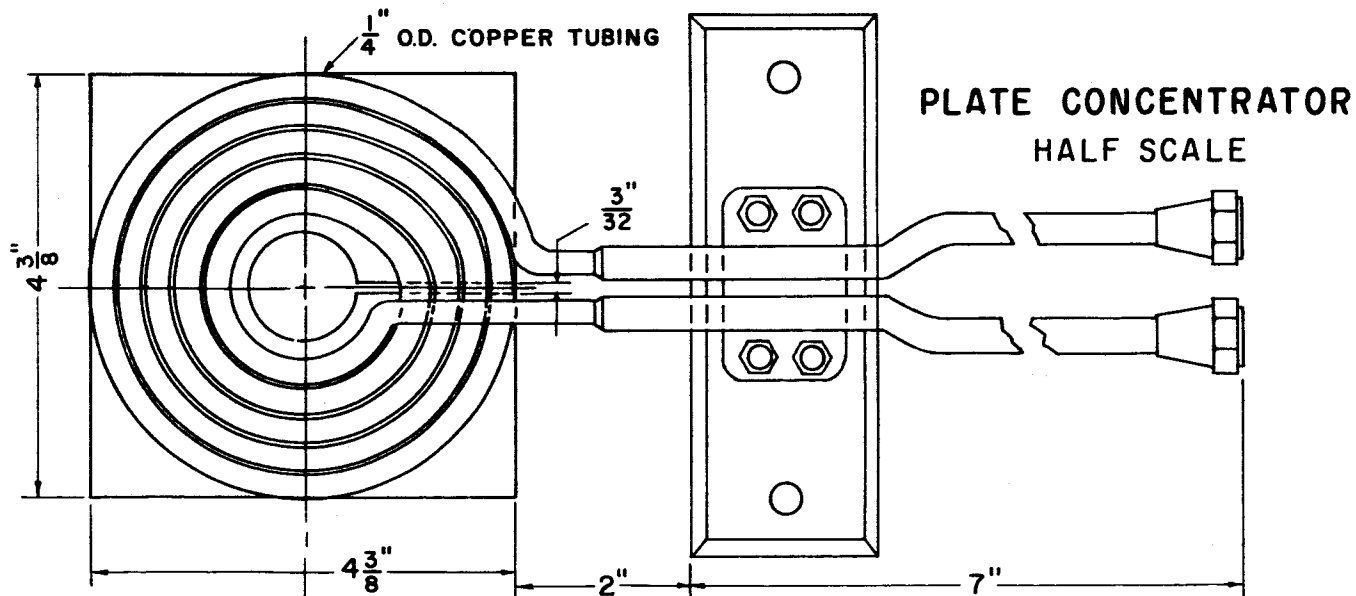
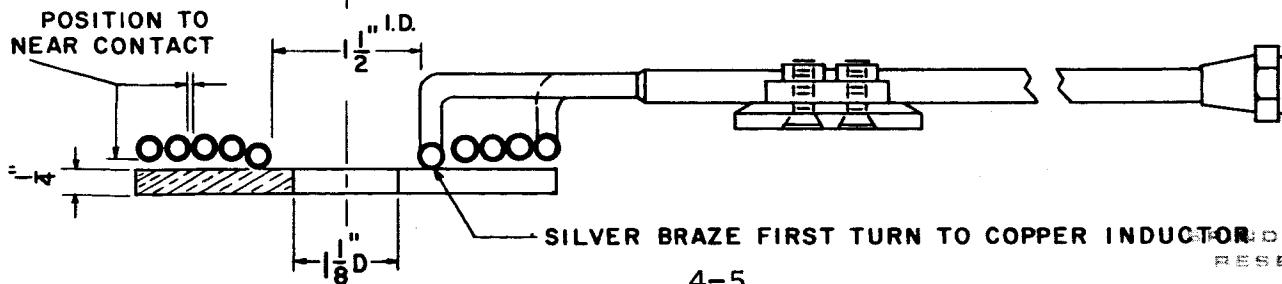


PLATE CONCENTRATOR  
HALF SCALE



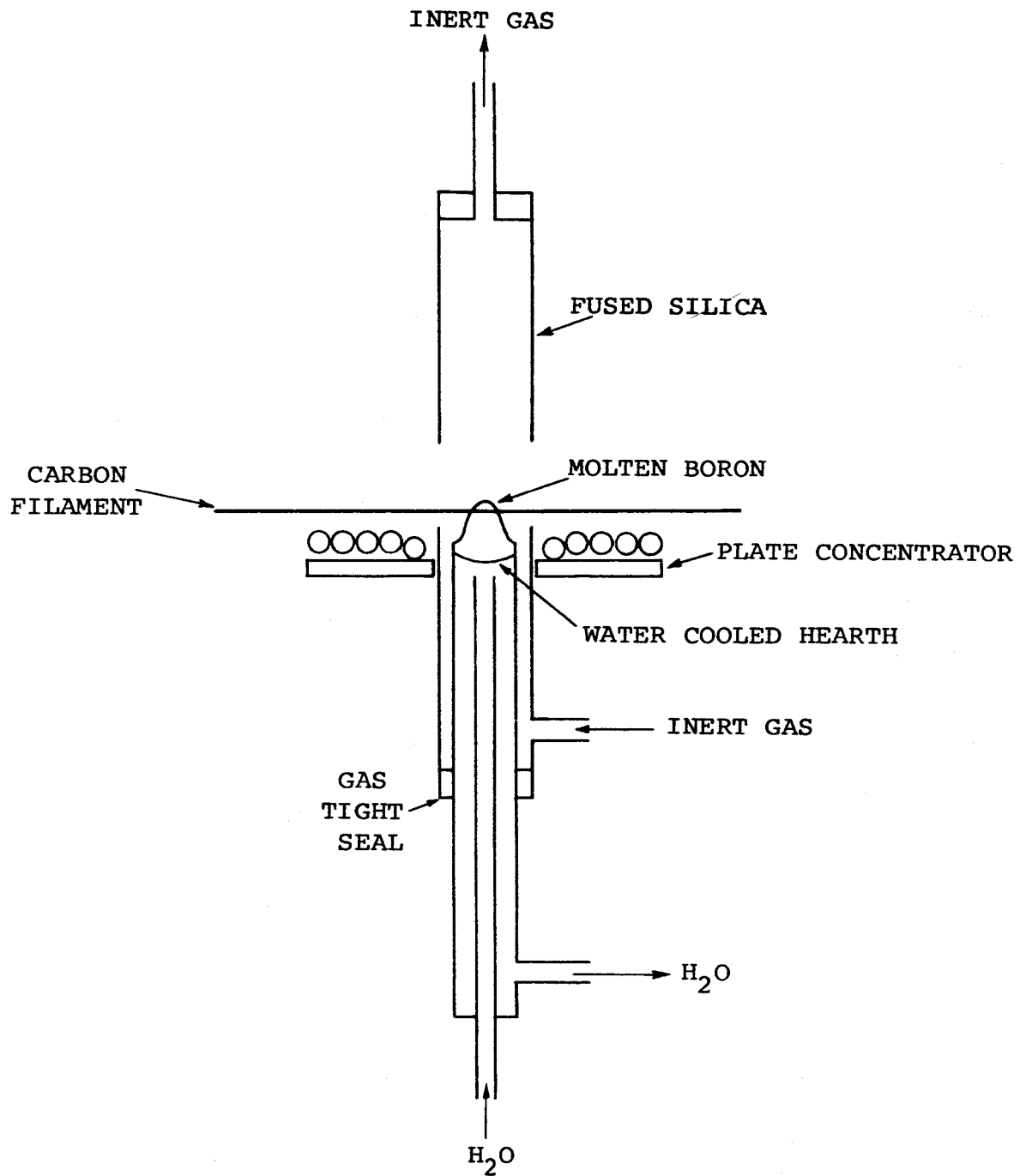


FIGURE 3. MELTING APPARATUS SCHEMATIC

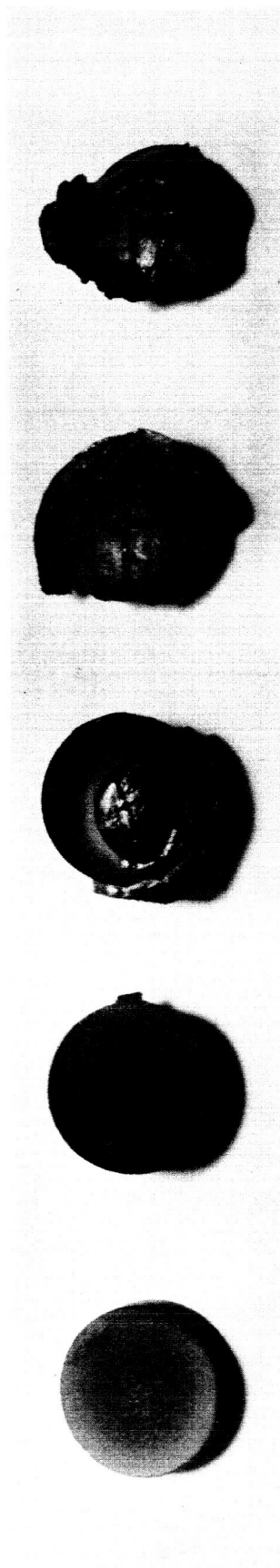
The first experiment with this apparatus consisted of stacking three boron carbide discs on the hearth with the uppermost disc centrally located in the horizontal plane of the rectangular plate of the plate-concentrator coil. With this arrangement, it was possible to melt the uppermost disc and a portion of the middle disc within a few minutes. Efforts to melt a single disc positioned within the plate-concentrator were not successful with the disc resting on the cold hearth. It was found that with two discs it was possible to partially melt the uppermost disc. Based on these observations, it was concluded that the proximity of the hearth to the plate-concentrator "robbed" a substantial portion of the available flux when positioned for single disc melting. While this arrangement would be satisfactory for simply melting boron carbide on boron carbide, it was far short of the goal of melting on a cold hearth. It was reasoned that the degree of eddy current generation in the hearth could be reduced by breaking up the current generation path in direct analogy to the laminated armatures employed in rotating electrical machinery. Accordingly, a split hearth was constructed as shown in Figure 2. Experimentation with this hearth resulted in single disc melting on the first attempt. Furthermore, as evidenced by the photographs shown in Figure 4, a portion of the bottom part of the disc had actually melted in contact with the cold hearth -- as evidenced by the imprint of the cold hearth grooves.

Figure 5 is a photograph of the actual melt. It is interesting to observe the bell shape the melt assumes as it rises above the plate-concentrator. The photographs given in Figure 6 show several representative samples of melts which did not penetrate through to the cold hearth.

The melting apparatus shown in Figure 3 was modified by slitting the fused silica tube downward along the cross-section diameter. This allowed for horizontal insertion of the fiber parallel to the plate-concentrator. With this arrangement it was possible to slide a portion of the fiber through the melt. Partially coated fibers were obtained in this manner. One such fiber is shown in Figure 7 and a cross-section of the same fiber in Figure 8.

#### PHASE E

During the course of this program, it was decided not to overlook the possibility of megacycle frequency generators



BOTTOM



TOP

FIGURE 4. BOTTOM AND TOP VIEWS SHOWING BORON CARBIDE MELTS (ACTUAL SIZE) OF PROGRESSIVE PENETRATION TO THE COLD HEARTH. (From left to right, the first disc is partially melted on the top side. The third disc has partially melted through to the cold hearth as indicated by the split-hearth imprint. The fourth and fifth discs have completely melted on the hearth. Observe the full split-hearth imprints.)



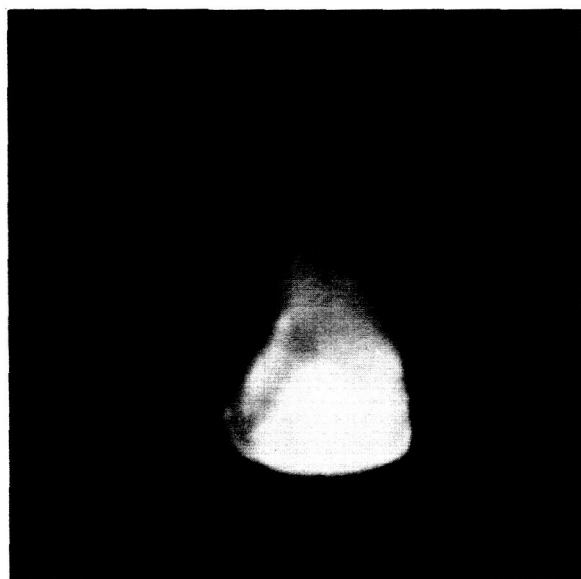
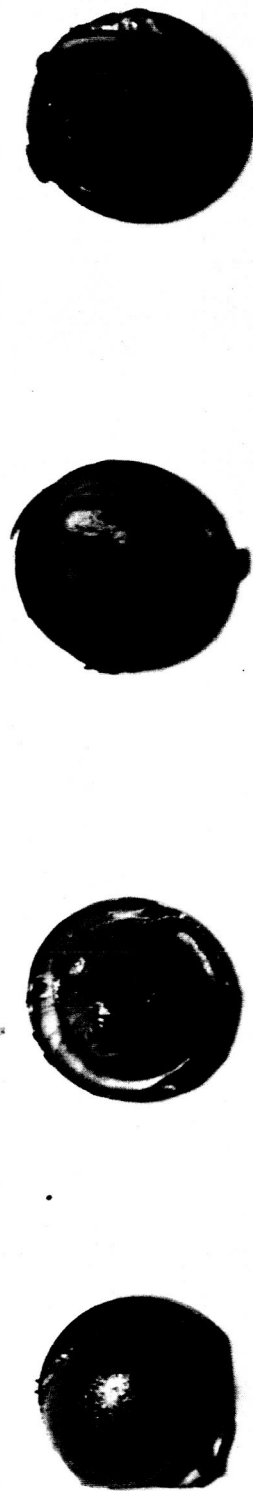


FIGURE 5. FRAME TAKEN FROM 8mm MOVIE FILM  
SHOWING THE BELL-SHAPED BORON  
CARBIDE MELT ON THE COLD HEARTH.



SIDE



TOP

FIGURE 6. SIDE AND TOP VIEWS SHOWING BORON CARBIDE MELTS (ACTUAL SIZE) WHICH DID NOT PENETRATE THROUGH TO THE COLD HEARTH.

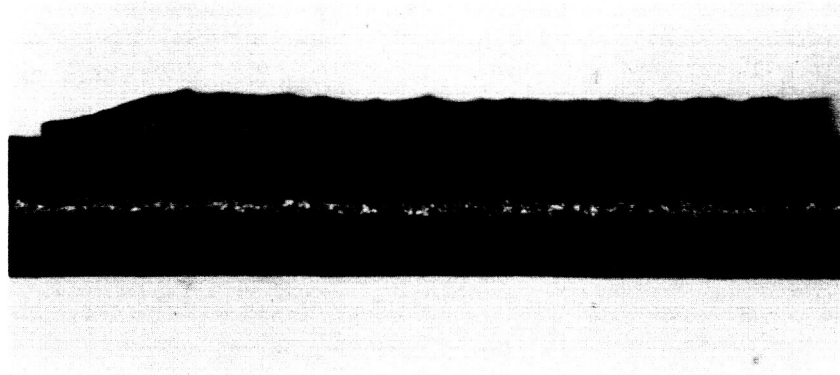


FIGURE 7. CARBON FIBER (0.006-IN. DIAMETER)  
PASSED THROUGH COLD HEARTH MELT OF  
BORON CARBIDE. MAGNIFIED 120 TIMES.  
(OBSERVE THE COATING ON THE UPPER-  
MOST FIBER PERIPHERY.)

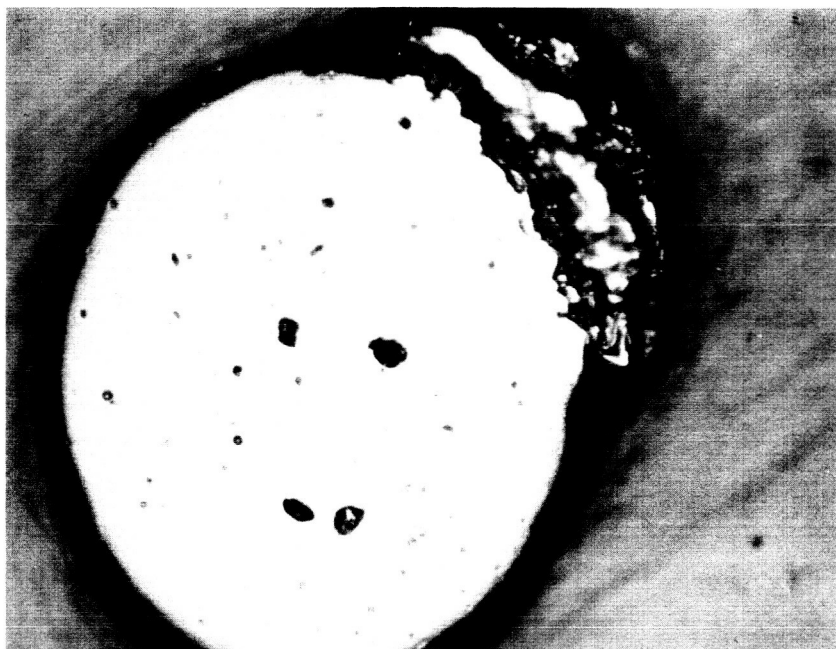


FIGURE 8. CROSS SECTION OF FIBER GIVEN IN  
FIGURE 7. MAGNIFIED 480 TIMES.

as a superior means of coupling to boron carbide. Accordingly, arrangements were made with Radio Frequency Company (7) to melt boron carbide discs on a water-cooled hearth in an inert atmosphere, using a frequency of 76 megacycles. This phase of the program was not intended to be exhaustive but rather to indicate the prospects that megacycle generators might afford. The results of these experiments revealed that coupling to the boron carbide was easy and subsequent melting was possible. However, at the frequency employed and with argon as the flush gas, plasma generation added certain difficulties, and this phase of the program was not pursued further.

## DISCUSSION

To achieve the objectives of this project it was necessary to melt boron carbide inductively on a water-cooled hearth and to pass a filament of carbon or graphite through the molten boron carbide and thereby coat it. Insofar as could be determined by literature research and communication with various laboratories (8) experienced in the melting of high-temperature compounds, boron carbide had not been previously melted inductively on a water-cooled copper surface. Early in the experimental program it was found that melting boron carbide on a water-cooled surface was a formidable problem. This problem eventually consumed most of the experimental effort and limited the time which could be devoted to the coating of the carbon filaments.

### PROBLEM ANALYSIS

Essentially, the problem is to provide either a conversion or deposition coating of boron carbide on a carbon filament as it is passed through the molten boron carbide. High strengths can probably be achieved if a microcrystalline coating is obtained. It was thought that the rapid quenching of the coated fiber as it passed through the melt into an inert atmosphere would be sufficient to produce the desired coating structure.

Consideration of boron carbon phase diagram in Figure 9 indicates that carbon is highly soluble in molten boron carbide at temperatures above  $2400^{\circ}\text{C}$ . Since the dissolution at these temperatures is probably extremely rapid, it was realized that it would be necessary to pass the filament through the liquid at a relatively high rate of speed. This was confirmed experimentally.

### MELT OBSERVATIONS

Some of the characteristics peculiar to the boron carbide melt obtained on the water-cooled hearth are worthy of mention. The onset of the melt is characterized by a mushrooming growth of liquid proceeding from an arbitrary point on the boron carbide disc surface. This liquid sheath eventually centers itself on the disc assuming a bell shape. In a spectacular fashion, this liquid blob oscillates back

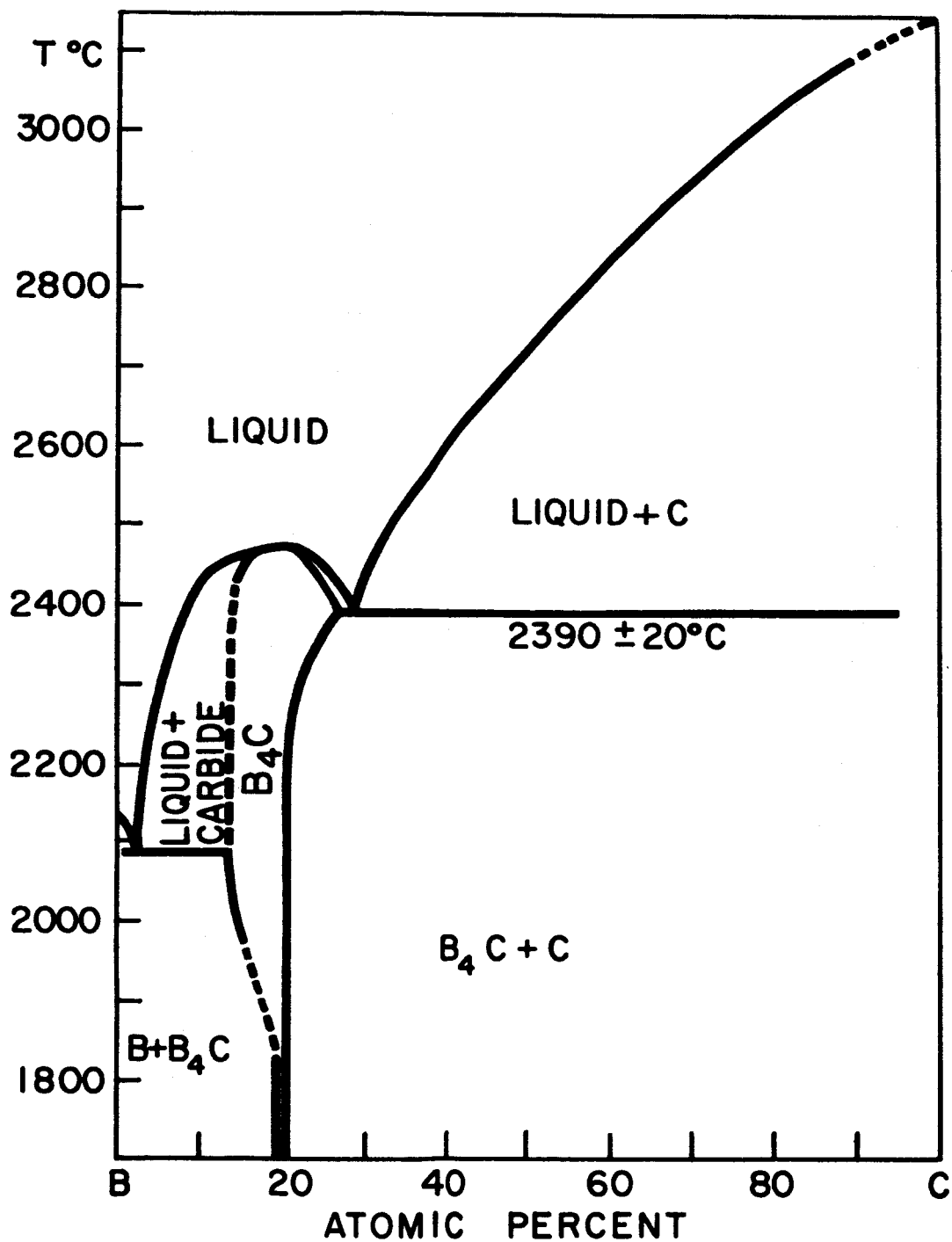


FIGURE 9. BORON-CARBON PHASE DIAGRAM  
(T.T. Dolloff WADD TR 60-143 July 1960)

and forth from the vertical while simultaneously rotating. The height that the melt reached was always about one inch above the plate-concentrator. Consideration of the relatively large volume occupied by the liquid melt indicated that the melt interior must be hollow. Examination of the cooled melts substantiated this hypothesis. A non-trivial practical advantage gained from the melt character is its height. Prior to these observations, it was thought that fiber entrance to the melt could only be obtained by drilling a passageway through the plate-concentrator. Now, however, it was only necessary to make entrance through the fused-silica tube well above the coil proper.

#### HEARTH CONSIDERATIONS

One problem associated with the boron carbide discs used in the experimental program is occasional cracking during the melt cycle. Even with the grooved hearth, the cracking is such that sufficient coupling to melt the disc is lost. However, if two discs are employed with the uppermost disc in the plane of the plate-concentrator, melting can always be obtained even if the disc cracks. This suggests that the split hearth as used here could probably be further improved to reduce current generation. Such modification might employ more cuts, possibly in the form of a criss-cross mat cutting. The extent of hearth splitting would probably have to be traded off with a subsequent decrease in the thermal conductivity of the hearth.

#### SOLUBILITY CONSIDERATIONS

From consideration of the phase diagram, it is reasonable to suppose that the solubility of the carbon filament would be less in a solution of boron carbide saturated with carbon than in a dilute solution of carbon in boron carbide. This carbon concentration effect is shown clearly in Figures 1 and 10 which compare the relative tapering of 1) a fiber immersed in a graphite crucible melt of boron carbide for about one second (Figure 1), and 2) a fiber placed in a boron carbide melt on a water-cooled copper hearth for one second (Figure 10).

The more gradual tapering of the fiber (shown in Figure 1) when immersed in a melt saturated with carbon, indicating a considerably slower rate of dissolution. Further, note in Figure 10 the rapid dissolution of the fiber immersed in a melt relatively low in free carbon.



FIGURE 10. CARBON FIBER (0.006-IN. DIAMETER)  
PLACED IN COLD HEARTH MELT OF BORON  
CARBIDE FOR APPROXIMATELY ONE SE-  
COND. MAGNIFIED 120 TIMES.



## DWELL-TIME CONSIDERATIONS

This phase of the experimental program has indicated that boron filaments of 0.006-inch diameter can be coated by passing the filament through molten boron carbide. The experimental program has also illustrated that the dwell time of fiber within the melt is a major process variable. The photographs given in Figures 7 and 10 illustrate two extremes of dwell time. The coating condition shown in Figure 7 was obtained by passing a six-inch length of fiber through the melting apparatus in approximately half a second. Of this six-inch length, approximately one inch of fiber contacted the melt corresponding to a dwell time of about 0.09 seconds. We assume that the boron carbide coating thickness is inversely proportional to the fiber velocity through the melt. This follows from the fact that reactions that take place between substances in different states occur at the boundary; that is, the surface between the phases. Therefore, for a given melt at a given temperature, the reaction depth per unit length of fiber must be directly proportional to the dwell time of the fiber within the melt and hence inversely to the fiber velocity. For example, if we are able to coat a 0.006-inch D fiber to a given thickness at a velocity of one foot per second, the same ratio of coating thickness to fiber diameter could be accomplished at six feet per second for an 0.0010-inch fiber, at 60 feet per second for an 0.0001-inch fiber, etc.

Still another factor influencing the dwell time is the cross-section length of melt through which the fiber passes. It is reasonable to assume that this width must vary as the diameter of the boron carbide disc and hence as the diameter of the plate-concentrator hole. Unlike the conventional coils employed in induction generators, the plate-concentrator working diameter is not limited by the radius of curvature that a copper tube may be made to assume. Consequently, it is conceivable that boron carbide could be melted on a cold hearth with considerably smaller dimensions than obtained in this program.



## RECOMMENDATIONS

1. Continue work to exploit the dwell-time kinetics of boron carbide melts on a water-cooled hearth as it influences coating thickness and fiber-melt reactivity.
2. Continue development of cold-hearth production of boron carbide-coated carbon fibers and broaden the scope of the work to include the use of fibers other than carbon.
3. Apply for patent covering the concept of carbon filament coating with boron carbide.
4. Publish technical article describing the developed technique for inductively melting boron carbide on a water-cooled hearth.

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3. Obtained from the Carborundum Company, Niagara Falls, New York
4. Load Coil Transformer Type L CT-4 obtained from Lepel High Frequency Laboratories, Inc., 55th Street and 37th Avenue, Woodside 77, New York City, N. Y.
5. Obtained from F. J. and J. Planchon  
78, rue la condamine  
Paris, France
6. Obtained from the Carborundum Company
7. Radio Frequency Company, Inc., 44-46 Park Street, Medfield, Massachusetts
8. Private communications with:
  - (a) N. H. Krikorian  
Los Alamos Scientific Laboratory  
Los Alamos, New Mexico
  - (b) John Niesse  
The Carborundum Company  
Research & Development Laboratory  
Niagara Falls, New York
  - (c) Lawrence Litz, John Criscione, and Raymond Serra  
National Carbon Company  
Division of Union Carbide & Carbon Company  
Research Laboratory  
Parma, Ohio